

## PATENT ABSTRACTS OF JAPAN

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(54) Co BASED ALLOY FOR LIVING BODY AND PRODUCTION METHOD THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a Co based alloy which has excellent wear resistance, and is suitable as a prosthetic material for artificial coxae, or the like.

SOLUTION: The Co based alloy for the living body has a composition containing, by mass, 26 to 30% Cr, 6 to 12% Mo and 0 to 0.3% C, and the balance substantially Co, and has a structure in which a granular second phase is finely dispersed into a matrix consisting of crystal grains having the average crystal grain size of  $\leq 50 \mu\text{m}$ . The alloy is produced by subjecting a Co based alloy having a prescribed composition to rapid cooling casting by using a water cooled mold made of copper, and subjecting the obtained ingot to forging at 1,000 to 1,300°C. In this way, its structure is controlled to the one where a granular second phase is finely dispersed into a fine structure, so that the alloy exhibits exceedingly excellent wear resistance.

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**CLAIMS**

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[Claim(s)]

[Claim 1] Cr: Co radical alloy for living bodies characterized by for 26 to 30 mass %, six to Mo: 12 mass %, C: 0.3 mass %, and the remainder having the presentation of Co substantially, and the second granular phase having the organization which did detailed distribution in the matrix which consists of crystal grain of 50 micrometers or less of diameters of average crystal grain.

[Claim 2] The manufacture approach of Co radical alloy for living bodies characterized by adjusting to the organization in which the second phase granular to the matrix which the diameter of average crystal grain become from the diameter of crystal grain 50 micrometers or less by carrying out quenching casting of the Co radical alloy which have a presentation according to claim 1 using water-cooled copper mold, and forging the obtained ingot 1000-1300 degrees C carried out detailed distribution.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is excellent in corrosion resistance, abrasion resistance, and workability, and relates to Co radical alloy for living bodies suitable as a prosthetic dentistry ingredient of an artificial aggregate, and its manufacture approach.

[0002]

[Description of the Prior Art] Although the object for casting of a Co-Cr system (HS-21), Vitallium, a Co-nickel-Cr-Mo alloy (MP35N) for processing (HS-25), etc. are known by the alloy for living bodies, since there are many clinical data and operating experiences and stability is high, Vitallium is used abundantly. Although Vitallium was developed as a dental alloy, the application has spread also to the orthopedics field through subsequent amelioration, and, otherwise, it is marketed by many trade names, such as Alivium, Endcast, Orthochrome, Orthochrome plus, Protasul, and Zimaloy. Although it is, since it excels in corrosion resistance and moreover has sufficient reinforcement and sufficient toughness rather than stainless steel, utilization of Vitallium is used as prosthetic dentistry ingredients for artificial hip joints, such as the condyle and a stem.

[0003] Vitallium for casting (HS-21) is a high Cr(30 mass %)-Co alloy containing Mo of 5 - 7 mass %, and it excels in corrosion resistance most also in Vitallium, and pitting, crevice corrosion, intergranular corrosion, stress corrosion cracking, etc. come out practically, and hardly pose a problem. However, it is easy to generate internal defects, such as a HIKE blow hole, air bubbles, and a segregation, and low fatigue strength (250MPa) is a fault. Vitallium for processing (HS-25) is the alloy improved so that the HIKE blow hole and segregation which are the fault of a casting might be canceled by replacing with Mo and permuting a part of Cr with nickel including W. Its plasticity more than annealing stainless steel is given by solution treatment, and, as for Vitallium for processing (HS-25), reinforcement comparable as the stainless steel for processing is given by cold working. Although corrosion resistance is superior to stainless steel, since it is not enough as a long-term object for implant, it is used for short term fixes, such as a bone plate and a wire.

[0004]

[Problem(s) to be Solved by the Invention] When making Mo content of Vitallium for processing increase, corrosion resistance and abrasion resistance improve. It is actually known that high Mo-Vitallium which increases the quantity of Mo to 10 mass % will present the corrosion resistance and abrasion resistance which were excellent at the beginning as compared with the alloy of a presentation. However, since the plastic workability of Vitallium falls with increase in quantity of Mo, it is hard to control the detailed organization of high Mo-Vitallium by the plastic-working method.

[0005] Canceling an internal defect is also examined by preparing the heat history by Vitallium for casting. Generally, crushing is carried out by forging, a dendrite organization is also destroyed, and the HIKE blow hole and air bubbles which have been produced in the casting alloy become a uniform organization by recrystallization annealing which follows. However, in Vitallium, sufficient knowledge is not acquired about change of the mechanical characteristics accompanying the relation of the heat history and the organization of a certain thing, and it is in the numerical data about improvement in mechanical characteristics. Therefore, although Vitallium is an ingredient which combines the stainless steel system excellent in workability with the advantage of both titanium system alloys excellent in properties, such as reinforcement and corrosion resistance, by the time need is low and widely put in practical use with about 20% of the whole, it will not have resulted.

[0006]

[Means for Solving the Problem] This invention aims at offering Co radical alloy for living bodies which is high

corrosion resistance and presents high abrasion resistance by carrying out organization adjustment by plastic working while it is thought out that such a problem should be solved and increases the quantity of Mo.

[0007] Co radical alloy for living bodies of this invention is characterized by for 26 to Cr:30 mass %, six to Mo:1 mass %, C:0 to 0.3 mass %, and the remainder having the presentation of Co substantially, and the second granular phase having the organization which did detailed distribution in the matrix which consists of crystal grain of 50 micrometers or less of diameters of average crystal grain in order to attain the purpose.

[0008] This Co radical alloy carries out quenching casting of the Co radical alloy of a predetermined presentation using water-cooled copper mold, and is manufactured by forging the obtained ingot at 1000-1300 degrees C.

[0009]

[Function] In this invention, the corrosion resistance of Vitallium and abrasion resistance are improved by increase in quantity and organization adjustment of Mo. Although the effectiveness of Mo exerted on corrosion resistance and abrasion resistance becomes remarkable above Mo:6 mass %, it is saturated with 12 mass % and Mo content an excessive amount has a bad influence on plastic workability. Although more than 26 mass % is required for C when securing corrosion resistance, the excessive amount exceeding 30 mass % has a bad influence on plastic workability. C content added if needed is regulated from a viewpoint made from abrasion resistance and plastic working below to 0.3 mass %.

[0010] In organization adjustment, by carrying out quenching casting using the copper mold of a water cooling type, growth of a sludge is suppressed and detailed distribution of the second phase of a sludge, an intermetallic compound, etc. is carried out by plastic working, such as elevated-temperature forging. The effect quenching at time of casting affects the growth suppression of a sludge becomes remarkable when cooling the temperature region from casting temperature to 400 degrees C with the above cooling rate by 1000-degree-C/. Moreover, cast structure such as a dendrite, is destroyed by elevated-temperature forging, and the matrix which consists of axial crystal grain, such as having been made detailed by 50 micrometers or less, is formed. Detailed-izing of a matrix is effective also in improvement in abrasion resistance. However, if the quantity of Mo content is increased only more than 6 mass %, since plastic workability, such as forging, will be lost, the forging alloy of high Mo-Vitallium cannot be manufactured.

[0011] In high Mo-Vitallium containing Mo more than 6 mass %, it applies to a low temperature side from the temperature field near 700 degree C, and a weak intermetallic-compound phase (sigma phase) generates. So, in this invention, generation of a sigma phase is prevented by selection of the heat treatment approach and working temperature. Specifically in this invention system which set Mo content as 6 - 12 mass %, elevated-temperature forging temperature is set as the range of 1100-1400 degrees C. Also when it has high Mo-Vitallium which carries out elevated-temperature forging in a room temperature and causes it, detailed distribution is carried out as a granular sludge or a crystallization object at a matrix, without preventing a sigma phase and the second phase growing by adopting quenching, such as water cooling.

[0012]

[Example 1] 600g of Co radical alloys with the presentation of Table 1 was dissolved with the RF vacuum melting furnace, the 15500-degree C molten metal was slushed into water cooling type copper metal mold, and quenching casting was carried out with the cooling rate (a part for 2300-degree-C/) which turns into temperature of 400 degrees C or less in 30 seconds. The tractive characteristics in the room temperature of material (as cast material) are shown in drawing 1 as [ each casting ]. In Co-Cr-Mo ternary alloy, elongation is improving, so that Mo addition increases. moreover, No. which carried out nickel addition -- 4 and 5 showed high elongation ductility.

[0013]

表 1 : 実施例で使用した各種 C o 基合金

試料 No.	合金成分及び含有量 (質量%)				
	Cr	Mo	Ni	C	Co
1	29	6	—	0.02	残部
2	29	8	—	0.02	残部
3	20	10	—	0.02	残部
4	20	10	16	0.02	残部
5	20	10	24	0.02	残部

[0014] The result of having investigated the effect of heat treatment exerted on elongation ductility about the allo of sample No.1 in which the smallest elongation ductility was shown in the condition of a casting as is shown in drawing 2 . Elevated-temperature forging of 1100 degrees C combines and shows the effect of heat treatment exerted on the same elongation ductility of sample No.1 which carried out organization adjustment for a comparison. as [ casting / which is not forging so that clearly from drawing 2 ] -- material -- the quenching effectiveness -- working -- \*\*\*\* -- as cast material and quenching material (they are 2-hour aging after and water quenching at 1050 degrees C) -- it was both low elongation ductility. Especially, the furnace-cooling material wh carried out furnace cooling after 1050-degree C aging treatment showed remarkable low elongation ductility. wit elevated-temperature forging, elongation ductility was boiled markedly and improved.

[0015] In order to investigate why elongation ductility is different between As cast material and furnace-cooling material, it gazed at each metal texture with the optical microscope. Although As cast material ( drawing 3 ) was metal texture where Mo Rich's b.c.c. phase deposited granular, in furnace-cooling material ( drawing 4 ), the sigma phase was growing in the shape of a straight line. It is guessed that it is a cause by which the low elongation ductility in a tension test is shown since a sigma phase is a brittle sludge which works as an origin of destruction. Moreover, in the elevated-temperature forging which showed high elongation ductility, a straight-line-like sigma phase was not detected but the granular b.c.c. phase had the organization which did detailed distribution.

[0016] When increase in quantity of Mo sets forging temperature as 1000 degrees C or more (preferably 1100 degrees C or more) at which the deposit of a sigma phase is suppressed instead of the direct cause which spoils th elevated-temperature forgeability of Co-Cr-Mo ternary alloy from elongation ductility and the relation of a metal texture and elevated-temperature forging is carried out, it turns out that Co radical alloy in which the outstanding elongation ductility is shown is obtained. Moreover, as a forging material, in order to control the deposit of a sigma phase, what carried out quenching casting using water cooling type copper mold is desirable. From the above res a paraphrase checked elongation ductility and that Co-Cr-Mo ternary alloy with good workability was obtained b controlling casting conditions and forging conditions. Then, the Co-Cr-Mo ternary alloy shown in Table 2 was ingoted, and the effect which quenching casting and elevated-temperature forging do was investigated.

[0017]

表 2 : 使用した C o 基合金

合金 No.	合金成分及び含有量 (質量%)					備 考
	Cr	Mo	Ni	C	Co	
1	19	10	31	0.02	残部	MP35N 相当
2	29	6	—	0.02	残部	標準的な Vitallium 相当
3	29	9	—	0.02	残部	高 Mo-Vitallium 相当
4	29	12	—	0.02	残部	高 Mo-Vitallium 相当

[0018] alloy No. -- after 1 and 2 carried out quenching casting with the cooling rate which turns into temperature 400 degrees C or less in 30 seconds after casting, they heated the ingot at 1100 degrees C, and carried out elevate temperature forging. When gazed at the metal texture after forging, it turned out that all are the crystalline structu

of equiaxed grain ( drawing 5 , 6). As for alloy No.1, the diameter of average crystal grain was [ the diameter of average crystal grain of about 100 micrometers and alloy No.2 ] about 50 micrometers. As a result of carrying out organization observation of alloy No.2, in alloy No.1, the second phase which was not detected had deposited or crystallized along the grain boundary. As for a sludge or a crystallization object, the crystal structure is considered to be Mo enrichment phase of b.c.c. from the result of the computational phase diagram of Thermo-Calc, and ED analysis. alloy No. -- about 3 and 4, heat treatment of 1100 degree-Cx 4 hours was performed, without forging an ingot. Observation of the metal texture after heat treatment gazed all at dendrite-like solidification structure ( drawing 7 , 8).

[0019] each -- the abrasion test was presented after carrying out the last polish finishing of the front face of the piece cut down from alloy No.1-4 with the wrapping film of No. 4000. In the abrasion test, an atmospheric-air ambient atmosphere and the amplitude of 10mm, the pin-on flat mold reciprocating motion abrasion testing machine which used alumina balls was used, it slid, and the distance of 200000mm, it slid and conditions with a rate of 8.33Hz were adopted. as compared with alloy No.1 of MP35N, abrasion resistance boiled alloy No.2-4 of Vitallium markedly, and was excellent so that the test result of drawing 9 might see. It can be said that it is not a best policy to add nickel from this by high concentration to Co-Cr-Mo the presentation of 3 yuan when securing high abrasion resistance although it is effective in respect of elongation ductility.

[0020] Furthermore, the result of having investigated the amount of wear of Vitallium about alloy No.2-4 in the detail is shown in drawing 10 . Since alloy No.4 were still solidification structure which contains Mo most, there were few amounts of wear. On the other hand, although alloy No.2 were an ingredient with few Mo contents, the were the amount of wear almost comparable as alloy No.4. Good abrasion resistance is the result of a detailed organization being adjusted by elevated-temperature forging in alloy No.2. That is, although abrasion resistance improves by increase in quantity of Mo, by adjusting an organization minutely shows improving further.

Subsequently, by carrying out elevated-temperature forging of the Co-Cr-Mo ternary alloy under the conditions which changed various forging conditions, such as forging temperature and rolling reduction, the diameter of crystal grain of a forging was changed and the effect the diameter of crystal grain affects the amount of wear was investigated. Abrasion resistance improved by detailed-ization of crystal grain, and the amount of wear decreased notably with 15 micrometers or less of diameters of crystal grain so that the results of an investigation of drawing 11 might see.

[0021]

[Example 2] 600g of Co radical alloys with the presentation of Table 2 of alloy No.3 was dissolved with the RF vacuum melting furnace, the 1550-degree C molten metal was slushed into water cooling type copper metal mold and quenching casting was carried out with the same cooling rate as an example 1. Organization adjustment was carried out by carrying out the clad of the obtained ingot with the hollow rod of SUS316L stainless steel, and carrying out elevated-temperature forging at 1100-1400 degrees C. By carrying out a clad with stainless steel, the direct contact to a forging tool and an ingot was avoided, and the ingot under forging has been held in the elevated temperature condition 1100 degrees C or more. Consequently, the deposit of a sigma phase has been prevented during elevated-temperature forging. Elevated-temperature forging annealing of -1250 degrees C was repeated until it became the thickness of 20mm including the clad plate, and finally water quenching was carried out after annealing of 1250 degree-Cx 2 hours.

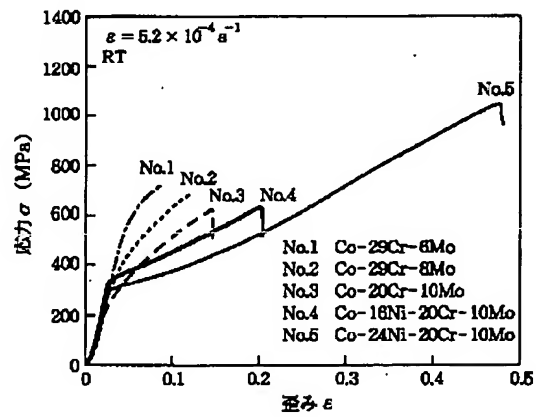
[0022] Subsequently, the forging was cold-rolled and the cold-rolled material of 5mm of board thickness was obtained. Concentrated hydrochloric acid: By immersing cold-rolled material in the mixed acid of concentrated-nitric-acid =3:1 (volume ratio), etching removal of the stainless steel in a cold-rolled material front face was carried out. Furthermore, annealing of 1250 degree-Cx 1 hour was given, and the web material of 50 micrometers of board thickness was manufactured with cold rolling for the second time after water quenching. This manufacture track record shows that Co radical alloy of this invention can be fabricated in the configuration where it was suitable for various artificial aggregates taking advantage of good workability.

[0023]

[Effect of the Invention] As explained above, Co radical alloy for living bodies of this invention carried out detailed distribution of the second phase by quenching casting, and has made the crystalline structure detailed with the elevated-temperature forging which suppressed generation of a sigma phase while it sets up many Mo contents with 6 - 12 mass %. Thereby, abrasion resistance is improved further and it is used as a charge of living body material for which the property which was excellent in Vitallium original is utilized.

[Translation done.]

Drawing selection drawing 1



[Translation done.]